PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 :
B05D 5/12, 3/02

A1

(11) International Publication Number: WO 99/16556

(43) International Publication Date: 8 April 1999 (08.04.99)

(21) International Application Number: PCT/US98/20494

(22) International Filing Date: 30 September 1998 (30.09.98)

(30) Priority Data:
60/060,436 30 September 1997 (30.09.97) US

(71) Applicant (*for all designated States except US*): PARTNERSHIPS LIMITED, INC. [US/US]; 32 Woodland Road, P.O. Road 6042, Lawrenceville, NJ 08648 (US).

(72) Inventor; and
(75) Inventor/Applicant (*for US only*): KYDD, Paul, H. [US/US]; 32 Woodlane Road, P.O. Box 6042, Lawrenceville, NJ 08648 (US).

(74) Agents: NISSIM, Stuart, H. et al.; Woodbridge & Associates, P.C., P.O. Box 592, Princeton, NJ 08542-0592 (US).

(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, HR, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Published
With international search report.

(54) Title: METHOD FOR METALLIZING HOLES

(57) Abstract

A composition of matter is disclosed which can be used to metallize component mounting holes and vias in circuit boards by a simple apply-and-heat process. The metallizing material is injected into the holes with a specially shaped needle. In an alternative method, the material is used to fill the holes, and the excess is sucked or blown out of the holes before heating and curing.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece			TR	Turkey
BG	Bulgaria	HU	Hungary	ML	Mali	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MN	Mongolia	UA	Ukraine
BR	Brazil	IL	Israel	MR	Mauritania	UG	Uganda
BY	Belarus	IS	Iceland	MW	Malawi	US	United States of America
CA	Canada	IT	Italy	MX	Mexico	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NE	Niger	VN	Viet Nam
CG	Congo	KE	Kenya	NL	Netherlands	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NO	Norway	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	NZ	New Zealand		
CM	Cameroon			PL	Poland		
CN	China	KR	Republic of Korea	PT	Portugal		
CU	Cuba	KZ	Kazakstan	RO	Romania		
CZ	Czech Republic	LC	Saint Lucia	RU	Russian Federation		
DE	Germany	LI	Liechtenstein	SD	Sudan		
DK	Denmark	LK	Sri Lanka	SE	Sweden		
EE	Estonia	LR	Liberia	SG	Singapore		

METHOD FOR METALLIZING HOLES

Background of the invention

Printed circuit boards are made by etching copper foil which is laminated to polymer-based sheets of insulation, typically epoxy-glass. Components are secured to the electrical traces thus created by inserting the wire leads of the components through holes drilled through the traces and the board and soldering them. In some cases it is desired to connect traces from one side of the board to the other via a hole even with no component lead. This is particularly true of multilayer boards in which the laminate consists of many layers of thin epoxy-glass, each with circuitry on both sides, and bonded together with thin sheets of prepreg between them.

A conventional method of interconnecting the conductive layers of multilayer printed circuit boards and the like consists of plating the walls of the hole with an electrically conductive material. The plating connects the exposed edges of the conductive layers. This operation consumes considerable time.

In all cases, the first step in interconnecting single-sided, double-sided and multilayer boards is to drill a pattern of holes to serve as vias and through-hole component connections. Multilayer boards need to be "desmearded" to remove melted epoxy from the exposed copper in the bore of the hole to permit a good electrical connection to be made to each exposed layer. The second step is to metallize the bores of the holes to create an electrical pathway covering the entire exposed surface. The third step is to build up the thickness of the metal in the holes by electroplating. These plated-through holes provide rugged and reliable connections through the board and to buried circuitry penetrated by the drill.

There are many prior art methods for the application of a metal coating to a hole in an electrically non-conductive, i.e., dielectric, surface in order to produce

circuit connections which will conduct an electrical current in accordance with the patterns of conductive metal circuits on the boards surface. These methods involve three basic steps: (1) treating the surface of the substrate with an agent to make it catalytically receptive to electrolessly-formed metal deposits; (2) electrolessly depositing a metal on the surface of the treated substrate; and (3) electrodepositing a plating metal over the electrolessly-formed metal deposits.

In typical processes associated with printed circuit board manufacture wherein through-hole metallization is employed, the catalytic material most often comprises palladium metal. The process of applying the catalytic material to the substrate surfaces typically involves contact of the surfaces with a true or colloidal solution of palladium and tin compounds. See, e.g. U.S. Pat. Nos. 3,011,920 and 3,532,518. In most cases, catalysis of the substrate surface is followed by an acceleration step which exposes or increases exposure of the active catalytic species.

Following deposition of the catalytic material on the hole surface, the surface is electrolessly plated by contact with an aqueous metal solution in which plating by chemical reduction leads to the deposit of metal from the bath onto the catalyzed surface. The through-holes are usually plated with a copper reduction procedure known to the art as electroless copper plating, such as that described by Clyde F. Coombs, Jr. in *Printed Circuit Handbook*, 3rd Edition, McGraw-Hill Book Co., N.Y., N.Y., 1988, Chapter 12.5.

Methods of the type described above have proven to be expensive and demanding of strict process controls. Further limitations on the use of these processes result from the chemical susceptibility of the electroless metal layer, and by the required use of hazardous and toxic chemical agents. Efforts to overcome these disadvantages have met with only partial success in the past, and have brought with them their own disadvantages.

Recently a number of direct metallization processes have been developed which eliminate the electroless plating step. These chemically deposit a thick enough

layer of conductive material that they can be electroplated directly. Palladium and carbon-loaded compositions have been commercialized.

Brief Summary of The Invention

The present invention, using PARMOD™ compositions, offers an alternative path to direct metallization which can put down a thick enough metal layer to eliminate electroless plating, and in many cases the electroplating process as well.

In carrying out the process of the present invention for the metallization of through-holes in printed circuit boards, any planar (rigid or flexible) circuit board material containing through-holes which require metallization can be employed. The circuit board to be treated can be a double-sided board, in which case the through-hole surfaces are composed solely of the material of the non-conductive substrate, or a multi-layer board, in which case the through-hole surfaces are comprised of alternating layers of non-conductive substrate and the exposed edges of metal (e.g., copper) inner layers. The non-conductive substrate material typically will be a glass-filled epoxy or a polyimide, but can in general be a suitable insulating thermosetting or thermoplastic material or combination thereof, including glass or fiber impregnated forms thereof, such as allyl phthalates, epoxy resins, polyesters, phenolics, acrylics, polyethylene, ABS terpolymers and the like. The process is applicable to any non-conductive substrate such as those recited above, inorganic materials such as ceramics, and the like. The invention also has applicability to the metallization of molded printed circuit boards such as those molded, for example, from polysulfones.

In a typical process for the metallization of through-holes, the substrate board material, such as copper-clad, glass-filled epoxy or copper-clad, flexible polyimide (e.g., DuPont Kapton) or multilayers of polyimide and adhesive-coated flexible polyimide, is provided with through-holes by drilling or punching, the holes are then scrubbed and de-burred. PARMOD™ compositions are then applied to the inner surface of the holes and cured to form consolidated metal conductors.

PARMOD™ mixtures contain a Reactive Organic Medium and metal flakes and/or metal powders. The ROM consists of either a Metallo-Organic Decomposition (MOD) compound or an organic reagent which can form such a compound upon heating in the presence of the metal constituents. The ingredients are blended together with rheology modifying organic vehicles well known in the art, if necessary, to produce printing inks or pastes. These inks can be printed on a temperature sensitive substrate and cured to well-consolidated, well-bonded electrical conductors at a temperature low enough so that the substrate is not damaged. The curing process occurs in seconds at temperatures far below those used for conventional sintering of thick film inks and pastes.

This fast, low temperature curing capability of PARMOD™ compositions, as well as their ready application, makes it possible to use them to metallize holes (vias) in circuit boards by very simple and low-cost processes. Two such processes are disclosed. In the first, individual holes are coated with PARMOD™ by injecting it with a specially modified needle. In the second PARMOD™ is applied to all the holes simultaneously, and the excess material is removed by blowing it or sucking it out of the holes. In both cases the PARMOD™ is thermally cured to a uniform coating of pure metal lining the bore of the holes.

Brief Description of the Drawings

Preferred embodiments according to the present invention will be described in detail with reference to the following figures, wherein:

Figure 1. is an illustration of the method of the invention using a modified needle for injecting composition into circuit board holes.

Figure 2 is a cross sectional view of a modified needle used in the method of the invention.

Detailed Description of the Invention

Preferred compositions useful for metallizing the holes are comprised of a metal mixture and a Reactive Organic Medium (ROM). These compositions can be applied to thermally stable substrates and cured to well-consolidated, pure metal conductor in the hole by heat treatment. The compositions exhibit a critical temperature above which they undergo a transformation to well-consolidated electrical conductors with a resistivity only two to four times the bulk resistivity of the metal in question. The electrical conductivity is equal to that obtained by conventional high temperature metal powder sintering in conventional thick film compositions on ceramic substrates. Remarkably, this consolidation process takes place at temperatures 400 to 500 degrees Celsius lower than with compounds conventionally used in thick film technology, and in times which are an order of magnitude shorter than are required for sintering.

Suitable metals include copper, silver, gold, zinc, cadmium, palladium, iridium, ruthenium, osmium, rhodium, platinum, iron, cobalt, nickel, indium, tin, antimony, lead, bismuth and mixtures thereof. Examples of typical proportions of PARMOD™ mixtures containing an organic acid as the ROM and both metal flakes and colloidal metal powder are illustrated in Table 1 as follows:

TABLE 1 **Acid-Based PARMOD™**

	Metal Flake	Metal Powder	Organic acid	Organic vehicle
Range	20-60%	10-45%	5-35%	0-35%
Preferred	40-60%	24-44%	5-20%	0-10%
Most preferred	40-60%	24-44%	10-20%	0-5%

Percents by total weight of the composition.

In a preferred embodiment, the metal mixture contains metal flake and colloidal or semi-colloidal metal powder where the total of flake plus powder is preferred to be 60-85% of the total mixture, and the powder is preferred to be 30-50% of the total metal. Larger amounts of organic vehicle may be added to reduce viscosity for certain applications.

The metal flakes have a major dimension between 2 to 10 micrometers, preferably about 5 micrometers, and a thickness of less than 1 micrometer. They can be produced by techniques well known in the art by milling the corresponding metal powder with a lubricant, which is frequently a fatty acid or fatty acid soap. The starting powders are usually produced by chemical precipitation to obtain the desired particle size and degree of purity. The flakes are sold for electronic applications as constituents of thick film inks and silver-loaded conductive epoxies.

The flakes perform several functions. They form a skeleton structure in the printed image which holds the other ingredients together and prevents loss of resolution when the mixture is heated to cure it. The flakes naturally assume a lamellar structure like a stone wall which provides electrical conductivity in the direction parallel to the surface of the substrate and provides a framework to lessen the amount of metal transport necessary to achieve the well-consolidated pure metal conductors which are the objective of this invention. They also provide low surface energy, flat surfaces to which the other constituents of the composition can bond.

The other metallic powder mixture constituent of the present invention are preferably colloidal or semi-colloidal powders with individual particle diameters below about 100 nanometers, preferably less than about 50 nanometers. The colloidal or semi-colloidal powder is preferably present in about 40% by weight of the total weight of the metal powder mixture. A primary function of these powders is to lower the temperature at which the compositions will consolidate to nearly solid pure metal conductors. The presence of fine metal powder has been found to be helpful in advancing this low temperature process with silver and essential to the consolidation of copper mixtures. It is important that they be present as individual particles. Metal

particles this small have a strong tendency to agglomerate into aggregates with an open skeletal structure.

Colloidal silver particles with a nominal diameter of 20 nanometers were shown to have an excellent state of dispersion and have been used in silver compositions and lowered the critical consolidation temperature from 300 to 260 degrees C.

To achieve and preserve the desired degree of dispersion of colloidal metal it is essential to stabilize the particles so that they cannot aggregate. In the case of the silver particles they were stabilized by the presence of a surfactant which coated the surface of the particles and prevented metal-to-metal contact. Suitable surfactants include carboxylic acids and metal soaps of carboxylic acids. This favors chemical precipitation as a means of producing the powders, since they can be exposed to an environment which promotes stabilization from formation to final consolidation.

The Reactive Organic Medium (ROM) provides the environment in which the metal mixture is bonded together to form well-consolidated conductors. Many classes of organic compounds can function as the ROM. The common characteristic which they share and which renders them effective is that they have, or can form, a bond to the metal via a hetero-atom. The hetero-atoms can be oxygen, nitrogen, sulfur, phosphorous, arsenic, selenium and other nonmetallic elements, preferably oxygen, nitrogen or sulfur. This bond is weaker than the bonds holding the organic moiety together, and can be thermally broken to deposit the metal. In most cases the reaction is reversible, so that the acid or other organic residue can react with metal to reform the metallo-organic compound, as shown schematically below:

I) $$R - M \Leftrightarrow R + M$$

where R is a reactive organic compound and M is the metal.

As an illustration of PARMOD™ mixtures containing MOD forming constituents such as organic acids, the reactions which take place in curing are as follows:

IIa.) Acid + Metal powder ⇒ MOD + H_2

or

IIb) Acid + Metal Oxide ⇒ MOD + H_2O

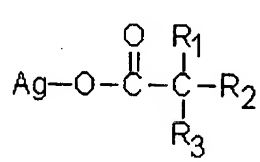
and

III) MOD + heat + H_2O ⇔ Bulk metal + Acid

The effect is to consume the small particles and weld together the big ones to create macroscopic circuit conductors of pure metal. In place of acid, some other active organic reagent which will produce an easily decomposed metallo-organic compound from either the oxide or the metal could be used. An example would be the use of sulfur compounds to make mercaptides or nitrogen ligands to produce decomposable complexes.

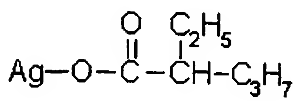
Examples of useful compounds are soaps of carboxylic acids, in which the hetero-atom is oxygen; amino compounds, in which the hetero-atom is nitrogen; and mercapto compounds, in which the hetero-atom is sulfur.

Specific examples of preferred ROM constituents are the carboxylic acids and the corresponding metallic soaps of neodecanoic acid and 2-ethyl hexanoic acid with silver and copper, such as. silver neodecanoate illustrated by the formula:

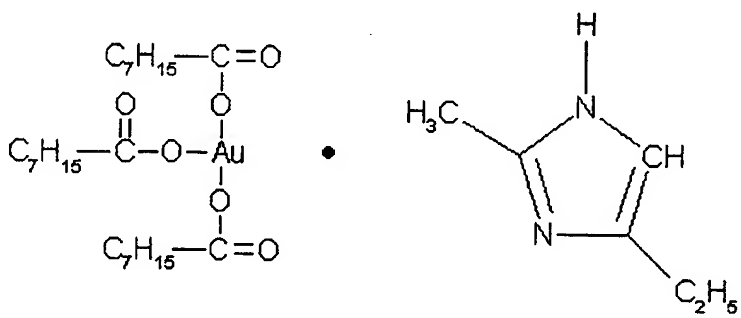


where R_1 + R_2 + and R_3 = C_9H_{19}

and silver 2-ethyl hexanoate as illustrated by the formula:

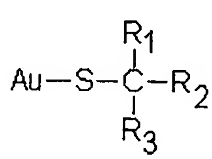


Gold amine 2-ethyl hexanoate is an example of a nitrogen compound.:



Gold amine 2-ethyl hexanoate (gold amine octoate)

Gold t-dodecyl mercaptide is an example of a sulfur compound:



where R_1 + R_2 + R_3 = $C_{11}H_{23}$

These ROM compositions can be made by methods well known in the art. All of the above compounds are capable of decomposition to the respective metals at relatively low temperatures. For the silver neodecanoate and silver 2-ethyl hexanoate (silver octoate), the decomposition temperature is between 200 and 250°C . For the corresponding copper compounds, it is between 300 and 315 C. Gold sulfides decompose at very low temperatures in the neighborhood of 150°C . Gold amine octoate decomposes between 300 and 500°C . The copper and silver compounds can be reformed from the corresponding acids at the same temperature, so the reaction is reversible, as mentioned above.

In some cases it is convenient to add rheology-enhancing compounds well known in the art to improve the printing characteristics of the compositions of the invention. Alpha-terpineol has been used to reduce the viscosity of copper and silver compositions to facilitate screen printing. Alpha-terpineol also participates in the consolidation reaction by virtue of the acid character of the OH group bonded to an unsaturated ring. By selecting constituents and additives, it has proven possible to produce a range of printable compositions ranging from fluid inks with a viscosity of 15 centipoise to solid powders.

Direct Injection

The most direct method by which PARMOD™ can be applied for metallizing holes in circuit boards is to directly inject it into the holes with a needle. Dispensing equipment is available for viscous materials such as PARMOD™ from EFD, East Providence, RI, among others. It consists of a syringe with a square ended needle which is pressurized with air to dispense the required amount of material. There are also more elaborate systems in which the material is pumped from the syringe through the needle by positive displacement or by a screw extruder. Such systems are offered by Asymtek and Camalot, among others.

It is preferred to apply a uniform coating approximately 0.05 mm (0.002 inch) thick to the bore of the hole. A simple square ended needle may not properly coat the

inside of a hole to metallize it. Either the hole may not be filled properly or it is completely filled may result in porous, uneven metallization due to evolution of gas during the PARMOD™ cure. In a preferred embodiment, the method employs the use of a needle in which the end is plugged and in which notches or holes are cut in the side of the needle barrel, as shown in Figure 1.

Tests performed with a single notch show that the two sides of the board can be connected, but the coating in the hole may not be complete. Using two notches in the needle is preferred, resulting in improved completeness of the coating. Three notches is even more preferable. Notches or slots are preferred over round holes, since they distribute the material into the bore of the hole more uniformly. The notches are preferably at the same height on the needle to prevent the majority of the material being injected from the notch nearest the material source. Notches are preferably spaced evenly around the circumference of the needle, e.g., 120°apart for three notches. Three slots have been cut to a depth of 0.007 inches in a needle with a wall thickness of 0.005 inches.

Holes have been coated in this way in a multilayer board approximately 1.5 mm thick with four layers. The holes were nominally 1 mm in diameter. Both a 20 gauge needle (0.91 mm outside diameter) with two notches and a 21 gauge (0.82 mm) needle with three notches have been used. The resulting coating was approximately 0.01 mm thick. Multiple component leads were successfully soldered into holes metallized in this way.

Multiple Hole Filling

The direct injection method may not be preferable when all the holes in a board, which may number in the thousands, are to be filled simultaneously. Unlike the case with microvias, which are small and shallow, high aspect ratio holes in rigid boards may not be successfully metallized by simply filling them with PARMOD™ paste, as mentioned above. However, if the excess material can be removed, this method can be used. This can be done by blowing or sucking the excess PARMOD™

material out of the holes, either while it is being applied or afterwards in a separate operation. Example of using vacuum to remove excess is disclosed by Ken Gileo in *Polymer Thick Film*, pages 58-62 (Van Nostrand 1996). An alternate method is to use surface tension forces to remove excess PARMOD™ material, such as, by blotting or using a porous backing strip underneath the board.

In one preferred embodiment PARMOD™ is applied to the drilled board with a squeegee or in some other way so as to ensure that all the holes are filled with PARMOD™ material. Any excess PARMOD™ could then be extracted by vacuum applied to the holes or by air pressure acting on the surface of the board with a relief behind the board to let the excess material pass through. This process could be performed immediately after drilling. Typically the boards are stacked three or more deep and drilled simultaneously with an aluminum entry plate and a backing plate to eliminate burrs in the circuit boards themselves. If the holes were drilled through the backing plate into a porous material PARMOD™ could be applied to the entry plate and sucked or blown through all the holes simultaneously. The boards could then be separated and thermally cured to convert the PARMOD™ to pure metal.

Examples

The examples described below indicate how the individual constituents of the preferred compositions and the conditions for applying them function to provide the desired result. The examples will serve to further typify the nature of this invention, but should not be construed as a limitation in the scope thereof. which scope is defined solely in the appended claims.

Example 1

A copper PARMOD™ ink was prepared by mixing 77 grams of nanometer sized spherical copper powder with 23 grams of neodecanoic acid in a glove box. This premix was than further mixed on a 2-roll mill for 30 minutes in air. The gap setting

on the mill was 0.006" - 0.008". After milling, the ink was removed from the mill and stored in a plastic syringe from which is also was dispensed.

The copper PARMOD^{TM} ink was applied to the inside walls of holes which had been drilled into rigid laminate with a 0.038" diameter drill. No adhesive was used in the holes prior to filling with the copper PARMOD^{TM} ink. The holes were filled by coating a 0.036" diameter needle with the ink, inserting and rotating the ink coated needle in the hole and than removing the needle. The injection process was repeated from the other side of the laminate. The laminate was than heat treated at 245^{o}C for 8 minutes in a N_2-H_2O-H_2 gas mix. The resulting filled holes were bright copper and conductive, and when coated with solder flux and dipped into a solder bath, the internal surface of the holes, coated with copper, in turn become coated with solder.

Example 2

Silver PARMOD screen ink was prepared by mixing together 12.0 grams of Degussa silver flake, 3.0 grams of silver neodecanoate, and 1.35 grams of neodecanoic acid using a spatula. The resulting mixture was then milled on roll mill to give a homogeneous paste.

Through holes in a 4-layer copper metallized FR-4 circuit board were metallized using the silver ink. The metallization was used to connect copper traces leading to the holes from the four separate layers. The ink was applied to the surface of the holes using a paste dispensing syringe system with a modified dispensing needle. The dispensing needle was modified by silver soldering the end closed and then cutting three slots in the side of the needle barrel, spaced at 120^{o}, approximately 0.025 inches wide and deep enough to intersect the needle bore. The ink could then be dispensed from the holes in the side of the needle barrel.

The circuit board with 0.038 inch diameter through holes to be metallized was mounted between two aluminum plates containing corresponding through holes. The circuit board assembly was then mounted on the XY plane of an XYZ table. The syringe from the paste dispensing system was mounted on the Z-axis arm of the table. A 21 gage modified dispensing needle was used with 80 PSI worth of pressure to dispense the silver ink. The dispensing needle was inserted into the through holes such that the ink was dispensed at the midpoint of the thickness of the circuit board. The ink was dispensed for 3 seconds into the through hole. The dispensing needle was then pushed through the hole before being pulled back out.

After all of the through holes were filled in this manner, the circuit board was removed from the assembly and any excess ink was wiped from the surface. The circuit board was then thermally treated at 260°C in air to convert the ink to pure silver with good adhesion in the holes. The silver coated the inside of the holes forming a "rivet-like" structure with the center of the hole remaining open.

Example 3

Copper PARMOD™ ink was prepared by mixing 31 grams of nanometer sized spherical copper powder with 38 grams of 9 micron diameter spherical copper powder, 15 grams of 3 micron diameter spherical powder, 14 grams of neodecanoic acid, and 2 grams of alpha terpineol in a glove box. This premix was then further mixed on a 2-roll mill for 30 minutes in air. The gap setting on the mill was 0.006" – 0.008". After milling, the ink was removed from the mill and stored in a plastic syringe from which it also was dispensed.

Copper PARMOD™ ink was applied to the inside walls of holes which had been drilled into rigid laminate with a 0.038" diameter drill. No adhesive was used in the holes prior to filling with the copper PARMOD™ ink. The holes were filled by coating a 0.036" needle with the ink, inserting and rotating the ink coated needle into the hole and then removing the needle. The laminate was then heat treated at 250°C

for 7 minutes in a N_2-H_20-H_2 gas mix. The resulting filled holes were bright copper and conductive, and when coated with solder flux and dipped into a solder bath, the internal surface of the holes, coated with copper, in turn become coated with solder.

While the invention has been described with reference to preferred embodiments thereof, it will be appreciated by those of ordinary skill in the art that modifications can be make to the structure and form of the invention without departing from the spirit and scope thereof.

What is Claimed

Claim 1. A method for metallizing holes in an electronic device comprising the steps of:

A). Placing a coating of a mixture comprising metal particles and a reactive organic medium containing a readily decomposable compound or a regent which can produce such a compound from the metal, on the inner surface of the holes; and

B). Curing the mixture with heat to deposit well-consolidated metallic conductors in the bores of the holes.

Claim 2. The method of claim 1 wherein said coating of said mixture is applied by injecting said mixture into the holes with a hollow needle,

said hollow needle having a barrel with a closed end and one or more openings in the side of said barrel.

Claim 3. The method of Claim 2 wherein said needle has 3 openings in the side of said needle.

Claim 4. The method of claim 2 wherein said openings in said needle are elongated slots.

Claim 5. The method of Claim 1 wherein the holes are coated by filling said holes with said mixture and removing excess mixture from the bore of the holes leaving a thin uniform coating.

Claim 6. The method of claim 5 wherein the excess mixture is removed by applying a pressure differential across the ends of the holes.

Claim 7. The method of claim 5 wherein the excess mixture is removed by surface tension forces.

Claim 8. The method of claim 1 wherein said readily decomposable compound in the reactive organic medium has a weak hetero atom bond to the metal such that it will decompose at a temperature which the electronic device.

Claim 9. The method of claim 7 wherein said hetero atoms are selected from the group consisting of: O, N, S, P, and As.

Claim 10. The method of claim 1 wherein the metal is selected from the group consisting of: the group IB, IIB, IVA, VA, VI A, VII A and VIIIA metals, indium, tin, antimony, lead and bismuth.

FIGURE 1

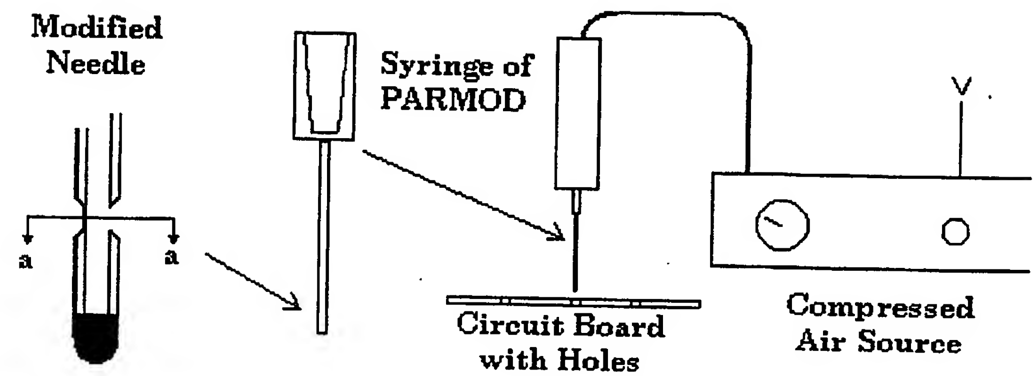
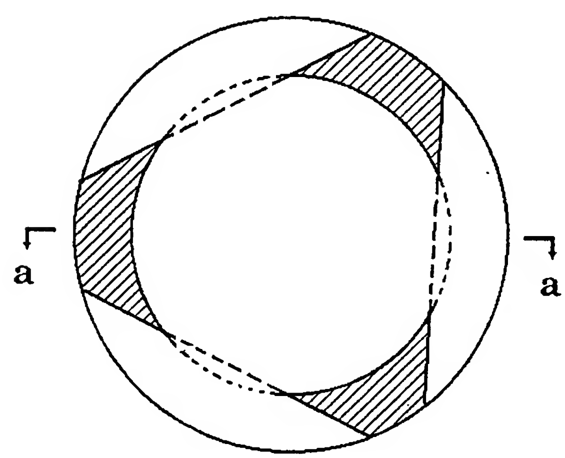


FIGURE 2



INTERNATIONAL SEARCH REPORT

International application No.
PCT/US98/20494

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) :B05D 5/12, 3/02
US CL :427/97,125,229,383.1

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 427/97,125,229,230,383.1

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

N/A

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

N/A

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 5,630,272 A (WENKE) 20 May 1997 (20-05-97), see abstract and col.4, lines 25 - col. 6, line 20	1-10
Y	US 5,356,658 A (HERTZ ET AL.) 18 October 1994 (18-10-94), see abstract and col. 2, lines 8-50	1-10
Y	US 4,544,577 A (MAY) 01 October 1985 (01-10-85), see abstract.	1-10
Y	US 3,576,669 A (FILIP) 27 April 1971 (27-04-71), see entire document.	1-10

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
10 NOVEMBER 1998	21 DEC 1998

Name and mailing address of the ISA/US	Authorized officer
Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231	BRIAN TALBOT
Facsimile No. (703) 305-3230	Telephone No. (703) 308-0661